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(54) Composite insect-proofing agent, insect-proofing method and package thereof.

(57) An insect-proofing product comprising trioxane and empenthrin.

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COMPOSITE INSECT-PROOFING AGENT, INSECT-PROOFING METHOD AND PACKAGE THEREOF

Background of the Invention

1. Field of the Invention

The present invention relates to a composite insect-proofing agent and insect-proofing method. More particularly, the present invention relates to a composite insect-proofing agent having an excellent effect of controlling harmful insects to clothes, and an insect control method using this composite insect-proofing agent. Moreover, the present invention relates to an insect-proofing agent package where the two effective ingredients volatilize or sublimate at a ratio which is substantially corresponding to the combination ratio of the two ingredients.

(2) Description of the Prior Art

Subliming substances such as camphor, napthalene and p-dichlorobenzene have heretofore been used as the insect-proofing agent for clothes.

However, camphor and naphthalene are insufficient in the controlling effects for harmful insects to clothes, such as a clothes moth and a carpet beetle, and p-dichlorobenzene involves problems concerning noxiousness and environmental pollution and it is required to reduce the amount used of this chemical.

Separately, insect-proofing agents comprising a pyrethroid chemical represented by (RS)-1-ethynyl-2-methylpent-2-enyl(1R)-cis,trans-chrysanthemate (hereinafter referred to as "empenthrin") have been developed and marketed.

However, the insect-proofing action of pyrethroid is not regarded as begin practically sufficient.

Furthermore, an insect-proofing agent comprising empenthrin and a subliming substance such as p-dichlorobenzene, naphthalene, camphor or 2,4,6-triisopropyl-1,3,5-trioxane is known (see Japanese Unexamined Patent Publication No. 61-83102 and Japanese Unexamined Patent Publication No. 62-72601). Since these subliming substances have a higher vapor pressure than empenthrin and have a high permeability to the packaging material, it is impossible to maintain a constant mixing ratio between the subliming substance and empenthrin. When 2,4,6-triisopropyl-1,3,5-trioxane is used as the subliming substance, the insect-proofing action is weak. In the foregoing patent publications, however, it is not taught or suggested that trioxane is used in combination with empenthrin.

We previously found that an insect-proofing agent comprising 1,3,5-trioxane (hereinafter referred to as "trioxane") as the active ingredient has a high insect-proofing effect (see Japanese Unexamined Patent Publication No. 63-115802). Even if trioxane is used singly, an effect of controlling harmful insects to clothes can be attained. If this insect-proofing effect can be enhanced, the amount used of trioxane can be saved.

Summary of the Invention

It is a primary object of the present invention to provide a composite insect-proofing agent showing a higher insect-controlling effect, a higher insectival harm-preventing effect and an insecticidal or repellent effect to harmful insects to clothes than the effects attained when respective ingredients are independently used, and an insect control method using this composite insect-proofing agent.

Another object of the present invention is to provide a composite insect-proofing agent exerting an excellent insecticidal effect with a small amount used, and an insect proofing method using this composite insect-proofing agent.

Still another object of the present invention is to provide an insect-proofing agent package in which a plurality of ingredients of a composite insect-proofing agent volatilize or sublimate at a ratio which is substantially corresponding to the mixing ratio of the ingredients and a synergistic insect-proofing effect by a plurality of the ingredients can be therefore manifested most efficiently, and the effective life of the composite insect-proofing agent can be prolonged.

In accordance with one aspect of the present invention, there is provided a composite insect-proofing agent comprising trioxane and empenthrin in combination as the active ingredients.

In accordance with another aspect of the present invention, there is provided an insect proofing method which comprising making trioxane and empenthrin as the active ingredients co-present in an atmosphere where insects to be controlled are present.

In accordance with still another aspect of the present invention, there is provided an insect-proofing agent package comprising a packaging material comprising an ethylene polymer film having many gas-permeable openings or a laminate film comprising said ethylene polymer film and a porous substrate and a composite insect-proofing agent comprising trioxane and empenthrin in combination as the active ingredients, which is contained within the packaging material.

Brief Description of the Drawings

Fig. 1 is a sectional view showing an applying tool for using trioxane and empenthrin in different preparation forms contained in different packages, respectively.

Fig. 2 is a sectional view showing a package for containing trioxane and empenthrin in different preparation forms in one package.

Fig. 3 is a sectional view showing a package in which a homogeneous mixture of trioxane and empenthrin is contained in one package.

Fig. 4 is a sectional view showing a package in which trioxane and empenthrin are contained in the form of liquid-supporting solid particles in one package.

Fig. 5 is a sectional view showing a package in which an insect-proofing agent comprising trioxane and empenthrin is double-packaged.

Detailed Description of the Preferred Embodiments

In the present invention, trioxane (1,3,5-trioxane) and empenthrin [(RS)-1-ethynyl-2-methylpent-2-enyl-(1R)-cis,trans-chrysanthemate] are used as the active ingredients. It is known that trioxane and empenthrin exert an insect-proofing effect independently when used singly. However, it is quite surprising that when they are used in combination, there can be attained a much higher insect-proofing effect than the effect attained when they are used singly.

In the present invention, by "making trioxane and emperithrin co-present in an atmosphere", it is meant that they are made co-present in such a large space that a vapor of trioxane and a vapor of empenthrin are mingled with each other. Practically, the interiors of a cabinet, a drawer, a wardrobe, a wardrobe warehouse and the like are meant by such an atmosphere. The atmosphere can be an open space, so far as vapors of trioxane and empenthrin are mingled with each other.

In the present invention, the combination of trioxane and empenthrin as the effective ingredients includes the combined use of them in different preparation forms and the combined use of them in the form of a single preparation of a mixture of them.

In the case where the active ingredients are used in different preparation forms, empenthrin is used in the form of an empenthrin-containing preparation obtained by making empenthrin support on a fibrous carrier such as a nonwoven fabric or a woven fabric or paper, an inorganic carrier such as a silica gel, an alumina gel, a zeolite, a foamed perlite or a foamed glass bead or an organic carrier such as a foamed or unfoamed polymer or rubber particle, a porous molded body or a polymer gel. On the other hand, trioxane can be used in the form of a solid preparation such as a powder, a granule, a tablet or a molded body. It is preferred that the trioxane preparation and the empenthrin-containing preparation be used while arranging them continuously or at small intervals. In a closed space, both the preparations can be separated from each other to such an extent that vapors of both the chemicals can be mingled with each other. It is preferred that the trioxane preparation be packaged with a porous packaging material such as paper and the porous packaging material be impregnated with empenthrin.

In the case where both the ingredients are used in the form of a single preparation, empenthrin is sprayed or coated on a powder, granule, tablet or other molded body of trioxane to hold empentrin on the solid trioxane preparation. Furthermore, a molded body can be obtained by adding empenthrin to melted trioxane to form a homogeneous mixture, casting the homogeneous mixture into a mold or vessel and cooling and solidifying the cast mixture. Moreover various solid preparations can be formed by subjecting

the above-mentioned mixture to pulverization and classification, granulation or tableting.

In the insect-proofing agent of the present invention, it is preferred that the amount of empenthrin be 0.02 to 2% by weight, especially 0.1 to 1% by weight. If the content of empenthrin is too high trioxane is lost by sublimation before empenthrin is lost by volatilization, or when they are used in the form of a mixture, empenthrin bleeds as the liquid from the packaging material. If the content of empenthrin is too low, empenthrin is lost by volatilization before trioxane is lost by sublimation, and the effect of enhancing the insecticidal action by the combined use is hardly manifested.

Of course, various addivites, for example, stabilizers such as antioxidants, ketoxims, hydrazin derivative and urea, excipients such as magnesium silicate, talc and starch, binders such as gum arabic, dextrin and CMC, carriers such as silica gel, perfumes and colorants can be added to the composite insect-proofing agent of the present invention according to need.

In order to control the sublimation speed of trioxane, it is preferred that trioxane or a mixture of trioxane and empenthrin be packaged with a synthetic resin film. In order to obtain a necessary sublimation speed of trioxane, gas-permeable openings can be formed in the synthetic resin film. A synthetic resin not damaged by the insect-proofing agent contained therein is used as the synthetic resin film. For example, there are preferably used films (plates and sheets are included; the same will apply hereinafter) of thermoplastic synthetic resins such as polyethylene, polypropylene, polyvinylidene chloride, polyvinyl alcohol, a polymethacrylate, a polyester, a polyamide and polyvinyl acetate. Furthermore, a semisynthetic resin film such as a cellophane film and a thermosetting synthetic resin film can be used. A laminate of the same kind of films or different kinds of films and a laminate comprising a film as mentioned above and a reinforcer such as paper, a woven fabric or a nonwoven fabric are preferably used. In the case where a high sublimation speed of trioxane is not particularly required, an unperforated film of a polyolefin, preferably polyethylene, especially preferably low-density polyethylene, can be used as the packaging material. The thickness of the film can be a thickness ordinarily adopted for packaging, and a thickness of about 20 to about 80 μm is preferable. At the practical application, the kind of the packaging material can be selected based on the ratio between empenthrin and trioxane.

We found that if an ethylene polymer film having many gas-permeable openings or a laminate film of this ethylene polymer film and a porous substrate is used as the packaging material for a composite insect-proofing agent comprising trioxane and empenthrin as the active ingredients, volatilization or sublimation of the active ingredients can be stably continued while maintaining the set ratio between the active ingredients, and a synergistic insect-proofing action by both the ingredients can be effectively attained over a long period of time. Namely, although empenthrin has a low volatilization speed, since empenthrin can permeate an ethylene polymer film, sufficient volatilization into the atmosphere can be attained. On the other hand, although trioxane has a high sublimation speed, the permeation through an ethylene polymer film is small and trioxane volatilizes into the atmosphere through gas-permeable openings formed in the film, and therefore, the volatilization speed of trioxane is effectively controlled by the openings.

As the olefin polymer, there can be used low-density polyethylene, medium-density polyethylene, high-density polyethylene, linear low-density polyethylene (LLDPE), an ethylene/propylene copolymer, an ethylene/butene-1 copolymer, an ethylene/propylene/butene-1 copolymer, an ethylene/propylene/unconjugated diene copolymer, an ion-crosslinked ethylene copolymer (ionomer), an ethylene/vinyl acetate copolymer, an ethylene/(meth)acrylic acid ester copolymer extended and unextended propylene polymer, buten polymer, and blends of two or more of the foregoing resins. In order to attain the objects of the present invention, low-density polyethylene (LDPE) or LLDPE is preferably used. The ethylene polymer film can be an unextended film (cast film) or a monoaxially or biaxially extended film.

In accordance with one embodiment of the present invention, a film having many through holes is used as the packaging material. The sublimation speed of trioxane can be adjusted by appropriately selecting the size and number of holes formed in the film layer on the surface of a synthetic resin film vessel and the total hole area (the area of whole holes per unit area of the effective surface of the synthetic resin film; the same will apply hereinafter).

The size of holes is preferably such that the effective diameter (the diameter of the hole regarded as a circle; the same will apply hereinafter) is about 0.5 to about 1.5 mm.

The number of holes is preferably 0.01 to 10 per cm^2 of the effective surface area of the synthetic resin film. The total hole area is generally 0.01 to 10 mm^2/cm^2. Incidentally, as this total hole area increases, the sublimation speed of trioxane increases.

In the present invention, the means for perforating the film layer is not particularly critical, and a customary method can be adopted. For example, there can be adopted a method in which a needle drum is pressed to the synthetic resin film vessel and a method in which the film layer is fused and perforated by using laser beams.

In accordance with another embodiment of the present invention, a filler-containing ethylene polymer film having fine open cells formed by drawing is used instead of the mechanically perforated film. It is known that if a filler such as silica or calcium carbonate is incorporated in a relatively large amount (20 to 60% by weight) into an ethylene polymer resin as mentioned above, the composition is formed into a film and the film is drawn, a porous film having fine open cells (0.1 to 5 μm in diameter) can be obtained. Also in the case where this porous film is used, the volatilization speeds of trioxane and empenthrin can be matched with each other.

Use of an ethylene polymer as mentioned above as the packaging material results in attainment of the following additional advantage. Namely, heat sealing can be easily performed at the bag-preparing or vessel-forming step.

Fig. 1 shows an embodiment in which a trioxane preparation and an empenthrin-containing preparation are used in the form of different preparations in different packages. A trioxane preparation-containing portion 2 and an empenthrin preparation-containing portion 3 are formed on a support 1 formed of a carton paper or plastic material. A solid trioxane preparation 5 packaged with a porous packaging film 4 is contained in the containing portion 2, and an empenthrin preparation 6 comprising a porous carrier impregnated with empenthrin, which is packaged with a gas-permeable film 7 if necessary, is contained in the containing portion 3. When the package shown in Fig. 1 is placed in a cloth cabinet or a drawer, the insecticidal action is manifested.

Fig. 2 shows an embodiment in which the trioxane preparation 5 and the empenthrin-containing preparation 6 are contained in different preparations in a single packaging material 8. As the packaging material 8, an ethylene polymer having gas-permeable openings or a laminate of this polymer film and a porous substrate (such as paper or a nonwoven fabric) is used.

Fig. 3 shows an embodiment in which a tablet 9 of a homogeneous mixture of trioxane and empenthrin is packaged with the above-mentioned porous film packaging material 8, and Fig. 4 shows an embodiment in which a composite insect-proofing agent comprising a powder or granule 5 of trioxane and an empentrin liquid preparation 6 held in the surface or grain boundary of the powder or granule 5 is packaged with the porous film packaging material 8.

The insect-proofing agent package of the present invention is supplied to consumers in the double-packaged state, that is, in the state where the outer side of the porous packaging material is packaged with a gas-impermeable packaging material. Fig. 5 shows an embodiment in which the package shown in Fig. 3 is further packaged with a gas-impermeable packaging material 10. As the gas-impermeable packaging material, there can be mentioned a transparent packaging material composed of a gas barrier resin such as an ethylene/vinyl alcohol copolymer or a vinylidene chloride copolymer and an opaque packaging material comprising an intermediate layer of an aluminum foil and films of a resin as mentioned above arranged on both the sides of the intermediate layer, it will be obvious to experts in the art that the package shown in Fig. 1, 2 or 4 can be double-packaged instead of the package shown in Fig. 3.

According to the insect proofing method of the present invention, trioxane and empenthrin are made co-present in an atmosphere where an insect to be controlled is present. According to the method of the present invention, trioxane is made present at a concentration of 0.3 to 10 mg/ℓ, preferably 1 to 6 mg/ℓ, in the above-mentioned atmosphere and empenthrin is made present at a concentration of 0.03 to 1 μg/ℓ, preferably 0.1 to 0.6 μg/ℓ, in the above-mentioned atmosphere.

The amount of the effective ingredients in the insect-proofing agent package of the present invention depends on the application place and the available period, but in general, when the insect-proofing agent package is used during a period of 120 to 180 days, the amount of the effective ingredients is preferably 20 to 100g.

The fact that a polyethylene film has a much higher empenthrin vapor permeability than other packaging materials is proved by the following Experiment 1.

Experiment 1

Each of bags having a size of 4.5 cm x 5.5 cm, which were composed of low-density polyethylene (referred to as "PE" hereinafter) having a thickness of 0.05 mm, a polyester (PET) film laminated with polyethylene, a nylon (NY) film laminated with polyethylene and a drawn film of polypropylene (PP) laminated with undrawn polypropylene, respectively, was charged with a filter paper having a size of 4 cm x 5 cm, which was impregnated with 0.2 g of empenthrin. The opening of the bag was heat-sealed and the sealed bag was allowed to stand still in a room maintained at a temperature of 35 ± 1 °C. For comparison, the operation was conducted in the same manner except that a filter paper having a size of 4 cm x 5 cm,

which was impregnated with empenthrin, was not charged in a bag. After 90 days, the weight decrease was measured. The obtained results are shown in Table 1.

Table 1

Packaging Material	Weight Decrease (mg)
PE	135
PET	8
NY	20
PP	30
unpackaged	135

The fact that the permeability of trioxane through a polyethylene film is much lower than those of other subliming substances even though the saturated vapor concentration of trioxane is much higher is proved by the following Experiment 2.

A bag having a size of 7 cm x 5 cm, which was formed of a low-density polyethylene film having a thickness of 0.04 mm, was charged with 2.0 g of a powdery sublimable substance shown below and the opening of the bag was heat-sealed. Then, the bag was hung in a room maintained at a temperature of 25 ± 1 °C. After 24 hours, the weight decrease was measured. The obtained results are shown in Table 2. For reference, the saturated vapor concentration of each sublimable substance at 25 °C is shown in Table 2.

Table 2

Chemical	Saturated Vapor Concentration (mg/ℓ)	Weight Decrease (mg)
trioxane	61.6	62
p-dichlorobenzene	7.9	758
naphthalene	0.6	95
(d,ℓ)-camphor	1.6	24

The present invention will now be described in detail with reference to the following examples that by no means limit the scope of the invention.

Example 1

A rectangular bag having a size of 10 cm x 6 cm, which was formed of a laminate film of Japanese paper (the base weight was 20 g/m^2) and a polyethylene film (the thickness was 30 µm), was charged with a mixture of 30 g of trioxane melted at 65 °C and 0.25 g of empenthrin and the opening of the bag was sealed. The bag was interposed between two stainless steel plates and was cooled to give flat solid and mold. Then, 6 holes were formed in the film layer by using a needle drum having many needles having a diameter of 0.5 mm, which were implanted on the periphery of the drum, whereby a package of a trioxane/empenthrin mixture was obtained.

Two packages of the trioxane/empenthrin mixture were prepared according to the above-mentioned procedures.

In a central portion of a clothes box made of polypropylene, which had an inner volume of 50 ℓ, the above-mentioned two packages of the trioxane/empenthrin mixture were placed at a position 5 cm apart from the bottom face so that the packages were separated from each other by 40 cm. Three net cages having a diameter of 3 cm, in each of which ten 40-days-old larvae of the case-making clothes moth (Tinea pellionella Linne) the clothes moth (30 mg/10 larvae) and a square woolen having a side of 3 cm (about 100

mg) were charged, were placed between the two packages.

The cloth box was allowed to stand still in a room maintained at 23 °C separated by a polypropylene film.

After 10 days, air in the dress box was sampled and the trioxane and empenthrin concentrations were measured by the gas chromatography, and the numbers of the living and dead moth larvae and the feeding damage quantity of the wool woven fabric were examined.

Furthermore, in an untreated control section, the experiment was carried out in the same manner without using any chemical.

The obtained results were evaluated based on the insect-killing ratio and the insectival damage ratio.

Namely, the insect-killing ratio X (%) was calculated according to the following formula:

$$X = \frac{\text{(death ratio in chemical-treated section)}}{\text{(death ratio in untreated control section)}}$$

The insectival damage ratio Y (%) was calculated according to the following formula:

$$Y = \frac{\text{(feeding damage quantity in chemical-treated reaction)}}{\text{(feeding damage quantity in untreated control section)}} \times 100$$

The death ratio was calculated according to the following formula:

$$\text{Death ratio} = \frac{\text{(number of dead insects)}}{\text{(number of tested insects)}} \times 100$$

Incidentally, no insects were killed in the untreated control section.

Comparative Example 1

Two packages were prepared in the same manner as described in Example 1 except that trioxane alone was used instead of the trioxane/empenthrin mixture, and the insect control test was carried out by using these packages in the same manner as described in Example 1.

Comparative Example 2

A rectangular filter paper having a size of 10 cm x 6 cm was uniformly impregnated with 0.25 g of empenthrin to obtain an empenthrin-impregnated filter paper.

Two empenthrin-impregnated filter papers were prepared according to the above-mentioned procedures, and the insect control test was carried out by using these filter papers instead of the package of the trioxane/empenthrin mixture in the same manner as described in Example 1.

The results obtained in Example 1 and Comparative Examples 1 and 2 are shown in Table 3.

Table 3

	Trioxane Concentratration (mg/ℓ)	Empenthrin Concentratration (μg/ℓ)	Insect-Killig Ratio (%)	Insectival Damage Ratio (%)
Example 1	2.5	0.3	63	10
Comparative Example 1	2.5	-	40	23
Comparative Example 2	-	0.3	17	14

Example 2

A square bag of a laminate film having a side of 8 cm, which was composed of a polyester film (30 μm in thickness) and a polyethylene film (15 μm in thickness) and in which 44 holes were formed by using a needle drum having a needle diameter of 0.5 mm, was filled with 30 g of granular trioxane having a particle size of 9 to 16 mesh to obtain a trioxane package. Separately, 0.1 g of empenthrin was uniformly impregnated on a rectangular filter paper having a size of 8 cm x 5 cm to obtain an empenthrin-impregnated filter paper.

In a central portion of a clothes box made of polypropylene having an inner volume of 50 ℓ, the above-mentioned trioxane package and empenthrin-impregnated filter paper were arranged in parallel and in contiguity each other at a position 5 cm above the bottom face, and five net cages having a diameter of 3 cm, in each of which ten 4-days-old larvae of the clothes moth (35 mg/10 larvae) and a square wool woven fabric (about 100 mg) having a side of 3 cm were charged, were fixed at a position 20 cm apart from the package and filter paper. Air in the dress box was sampled and the trioxane and empenthrin concentrations were measured by the gas chromatography.

The clothes box was allowed to stand still in a room maintained at a temperature of 23 °C separated by a polypropylene film.

After 10 days, the numbers of the living and dead larvae of the clothes moth and the insectival damage quantity of the woolen fabric were examined. Furthermore, in an untreated control section, the experiment was carried out in the same manner without using any chemical.

The obtained results were evaluated based on the insect-killing ratio and the insectival damage ratio in the same manner as described in Example 1. Incidentally, no larvae were dead in the untreated control section.

Comparative Example 3

The insect control test was carried out in the same manner as described in Example 2 except that the empenthrin-impregnated filter paper was not used but the trioxane-impregnated filter paper alone was used.

Comparative Example 4

The insect control test was carried out in the same manner as described in Example 2 except that the trioxane package was not used but the empenthrin-impregnated filter paper alone was used.

Comparative Example 5

A package of 2,4,6-triisopropyl-1,3,5-trioxane was prepared in the same manner as described in Example 2 except that 2,4,6-triisopropyl-1,3,5-trioxane was used instead of trioxane. By using this package and the empenthrin-impregnated filter paper the insect control test was carried out in the same manner as described in Example 2.

The results obtained in Example 2 and Comparative Examples 3, 4 and 5 are shown in Table 4.

Table 4

	Trioxane Concentratration (mg/ℓ)	Empenthrin Concentratration (µg/ℓ)	Insect-Killig Ratio (%)	Insectival Damage Ratio (%)
Example 2	3.8	0.2	80	10
Comparative Example 3	3.8	-	40	25
Comparative Example 4	-	0.2	35	50
Comparative Example 5	-	0.2	35	50

Example 3

A square bag composed of a laminate film of Japanese paper (20 g/m^2 and a polyethylene film (30µm in thickness) having a side of 8 cm, in which 8 holes were formed by using a needle drum having a needle diameter of 0.5 mm, was filled with 25 g of granular trioxane having a particle size of 9 to 16 mesh to obtain a trioxane package.

A reactangular filter paper having a size of 5 cm x 4 cm, which was uniformly impregnated with 0.1 g of empenthrin, was packaged with a laminate film having a size of 6 cm x 5 cm, which was composed of Japanese paper and a polyethylene film similar to hereinbefore, to obtain an empenthrin package. The trioxane package and empenthrin package were placed contigously to each other in an thermostatic chamber tank maintained at 30°C. The interior of the tank was ventilated with nitrogen gas.

The residual amounts of trioxane and empenthrin left after the lapse of a certain period are shown in Table 5. At the standing time of 80 days, trioxane in the trioxane package had been lost by sublimation, and empenthrin in the empenthrin package had been substantially lost by volatilization.

Table 5

Standing Time (days)	Residual Amount (g) of Trioxane	Residual Amount (g) of Empenthrin
0	25.00	0.10
60	6.08	0.02
80	0.00	0.01

Example 4

A square bag of a laminate film comprising Japanese paper (20 g/m^2) and a polyethylene film (30 µm in thickness) having a side of 8 cm, in which 60 holes were formed by a needle plate having a needle diameter of 0.5 mm, was filled with 20 g of granular-trioxane having a particle size of 9 to 16 mesh. An empenthrin-impregnated paper obtained by impregnating 0.05 g of empenthrin uniformly on a rectangular filter paper having a size of 7 cm x 5 cm was inserted in a space between the granular trioxane and the laminate film and the opening of the bag was heat-sealed, whereby an insect-proofing agent package was obtained. The effective area except the area of the sealed portion was 8 cm x 6 cm.

Two insect-proofing agent packages were prepared according to the above-mentioned procedures.

In a central portion of a cloth box made of polypropylene having an inner volume of 50 ℓ, the two insect-proofing agent packages were placed at a position 5 cm apart from the bottom face so that the packages were separated by 40 cm from each other. Three net cages having a diameter of 3 cm, in each of which ten 40-days-old larvae of the clothes moth (37 mg/10 larvae) and a square wool woven fabric (about 100 mg) having a side of 3 cm were fixed between the two packages.

This clothes box was allowed to stand still in a room maintained at a temperature of 23 to 25°C and a

relative humidity of 60 to 70%.

After 10 days, the numbers of living and dead larvae and the insectival damage quantity of the woolen fabrics were examined. In an untreated control section, the test was carried out in the same manner without using any chemical.

The obtained results were expressed by the insect-killing ratio and the insectival damage ratio. Incidentally, no larvae were dead in the untreated control section.

The obtained results are shown in Table 6.

Comparative Example 6

Two trioxane packages were prepared in the same manner as described in Example 4 except that the empenthrin-impregnated filter paper was not used and the granular trioxane alone was used. The insect control test was carried out in the same manner as described in Example 4 by using the obtained trioxane packages. The obtained results are shown in Table 6.

Comparative Example 7

Two empenthrin filter paper packages were obtained in the same manner as described in Example 4 except that trioxane was not used and the empenthrin-impregnated filter paper alone was used. The insect control test was carried out in the same manner as described in Example 4 by using the obtained packages. The obtained results are shown in Table 6.

Table 6

	Insect-Killing Ratio (%)	Insectival Damage Ratio (%)
Example 2	97	15
Comparative Example 3	70	19
Comparative Example 4	23	53

Example 5

A rectangular bag having a size of 9 cm x 5 cm, which was formed by pasting Japanese paper sheets, was filled with 25 g of granualr trioxane having a size of 9 to 16 mesh, and the bag was sealed. Then, 0.05 g of empenthrin was uniformly coated on the Japanese paper bag. Then, the bag was filled in a bag composed of an unperforated low-density polyethylene film haivng a thickness of 20 µm, and the film bag was heat-sealed to obtain a pacakged insect-proofing agent. The effective area except the area of the sealed portion was a rectangular area of 10 cm x 6 cm.

The packaged insect-proofing agent was placed at the center of a dress box having an inner volume of 50 at a position 5 cm apart from the bottom surface.

The dress box was allowed to stand still in a room maintained at a temperature of 22 to 23°C and a relative humidity of 50 to 60%.

After 10 days, air in the dress box was sampled and analyzed by the gas chromatography. It was found that the trioxane concentration was 2.5 mg/ℓ and the empenthrin concentration was 0.3 µg/ℓ.

Claims

1. An insect-proofing product comprising trioxane and empenthrin.
2. A product according to claim 1, wherein the empenthrin is present in an amount of from 0.02 to 2% by weight based on the weight of the trioxane.

3. A product according to claim 2, wherein the empenthrin is present in an amount of from 0.1 to 1% by weight based on the weight of the trioxane.

4. A product according to any one of claims 1 to 3, wherein the trioxane and the empenthrin are separately.

5. A product according to claim 4, comprising trioxane in the form of a powder, granules, or molded body such as a tablet, and a porous carrier impregnated with empenthrin.

6. A product according to any one of claims 1 to 3, wherein the trioxane and the empenthrin are present in a single preparation.

7. A product according to claim 6, which comprises a powder, granules or molded body such as a tablet, of a homogeneous mixture of the trioxane and the empenthrin.

8. A product according to claim 6, which comprises a powder or granules of trioxane, and empenthrin in the grain boundaries of the powder or granules.

9. An insect-proofing package comprising a packaging material comprising a gas-permeable plastic polymer film or a laminate of the polymer film with a porous substrate and a preparation as defined in any one of the preceding claims contained within the package.

10. A package according to claim 9, wherein the plastic polymer film has perforations.

11. A package according to claim 10, wherein the plastic polymer file is a polyethylene film.

12. A package according to claim 10 or 11 wherein the effective diameter of the holes in the plastic polymer film is from 0.5 to 1.5mm.

13. A package according to claims 10 to 12 wherein the number of holes in the plastic film is from 0.1 to 10 per cm^2 of the effective surface of the packaging material.

14. A package according to any one of claims 10 to 12, wherein the total hole area in the plastic polymer film is from 0.01 to $10mm^2$ per cm^2 of the surface area of the packaging material.

15. A package according to claim 9, wherein the plastic polymer film is a non-perforated polyolefin film.

16. A package according to claim 15, wherein the polyolefin film is a polyethylene film.

17. A package according to claim 10, wherein the plastic polymer film is a filler-containing extended plastic polymer film having fine open cells formed by extension.

18. A package according to any one of claims 10 to 17 which is further packaged with a substantially gas-impermeable film or a laminate thereof with an aluminium foil.

19. A method of controlling insects comprising releasing trioxane and empenthrin vapours into an atmosphere.

20. A method according to claim 19, wherein the trioxane and the empenthrin are present in the atmosphere in concentrations of from 0.3 to 10 mg/l and from 0.03 to 1 µg/l respectively.

21. A method according to claim 19 wherein the trioxane and the empenthrin are present in the atmosphere in concentrations of from 1 to 6 mg/l and from 0.1 to 0.6 µg/l respectively.

22. Use of trioxane and empenthrin in an insect control method.

23. A process for preparing a product as defined in claim 1 which comprises incoporating the trioxane and the empenthrin in the product.

Fig. 1

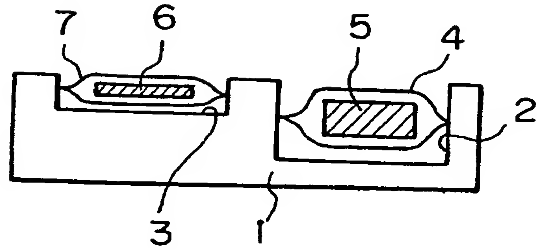


Fig. 2

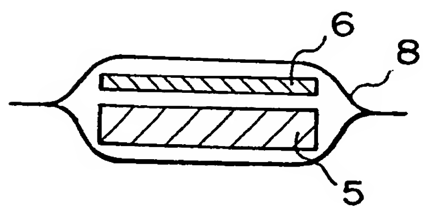


Fig. 3

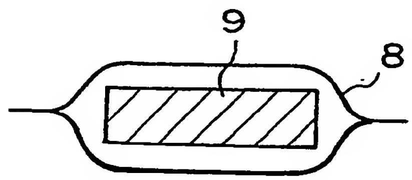


Fig. 4

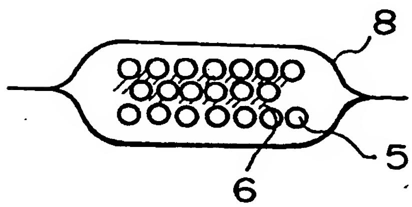
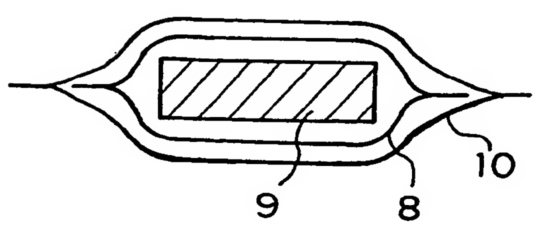


Fig. 5



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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 2523

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 269 292 (MITSUBISHI GAS CHEMICAL CO.) * Page 3 - page 4, line 52; claims 1,4,6,7,16,17 * & JP-A-63 115 802 (Cat. D)	1-23	A 01 N 25/18 A 01 N 53/00 // (A 01 N 53/00 A 01 N 43:32)
Y	CENTRAL PATENTS INDEX, BASIC ABSTRACTS JOURNAL, section C, week 8623, 30th July 1986, accession no. 86-147734/23, Derwent Publications, Ltd, London, GB; & JP-A-61 083 102 (OSAKA SEIYAKU K.K.)	1-23	
Y	PATENT ABSTRACTS OF JAPAN, vol. 11, no. 268 (C-444)[2715], 29th August 1987, page 111 C 444; & JP-A-62 072 601 (OSAKA SEIYAKU K.K.) 03-04-1987 (Cat. D)	1-23	
Y	US-A-3 364 105 (M. GEIGER) * Column 1, lines 10-44; examples 1a.1c; claim 1 *	1-23	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 275 (C-516)[3122], 29th July 1988; & JP-A-63 054 307 (IDEMITSU PETROCHEM. CO., LTD) 08-03-1988	1-23	A 01 N
A	US-A-4 123 525 (Y. UENO) * Column 1, line 10 - column 2, line 64; claim 1 *	1-23	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-06-1990	MUELLNERS W.

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